

Cubic-scaling algorithm and self-consistent mean field for random-phase approximation with second-order screened exchange

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(Dated: 18 March 2013)

The random-phase approximation with second-order screened exchange (RPA+SOSEX) is a model of electron correlation energy with two caveats: its accuracy depends on an arbitrary choice of mean field, and it scales as $\mathcal{O}(n^5)$ operations and $\mathcal{O}(n^3)$ memory for n electrons. We derive a new algorithm that reduces its scaling to $\mathcal{O}(n^3)$ operations and $\mathcal{O}(n^2)$ memory through controlled approximations and derive a self-consistent mean field that approximates Brueckner coupled-cluster doubles (BCCD) theory with RPA+SOSEX, referred to as Brueckner RPA (BRPA). The algorithm similarly reduces the scaling of second-order Møller-Plesset (MP2) perturbation theory with smaller cost prefactors than RPA+SOSEX. We test the new model's accuracy on the dissociation of H_2 .

The random-phase approximation (RPA) combined with second-order exchange models the correlation energy of the uniform electron gas in the high-density limit¹. For densities relevant to materials, this model is extended to second-order *screened* exchange (SOSEX) within coupled-cluster theory². RPA+SOSEX matches quantum Monte Carlo benchmarks on the uniform electron gas³ to within 0.002 Ha/electron. Further extension to finite and inhomogeneous systems is possible by combining the RPA+SOSEX model with Kohn-Sham orbitals and orbital energies within density functional theory⁴ (DFT). Benchmarks on finite systems⁵ show mean absolute errors of 0.012 Ha/atom for total energies of first and second row atoms and 0.008 Ha/molecule for atomization energies of molecules in the G2-1 test set. Unfortunately, B3LYP-based DFT is more accurate than RPA+SOSEX, even after further corrections⁶. It is unclear whether the dominant source of error is the use of a Kohn-Sham mean field or the RPA+SOSEX model itself. The optimal RPA+SOSEX mean field is as yet unknown.

Despite a growing interest⁷⁻⁹ in RPA methods, including RPA+SOSEX, DFT remains the computational workhorse of electronic structure theory because of the high cost and poor scaling of RPA calculations. DFT requires $\mathcal{O}(n^3)$ operations and $\mathcal{O}(n^2)$ memory for n electrons, while $\mathcal{O}(n^5)$ operations and $\mathcal{O}(n^3)$ memory are required by RPA+SOSEX. Even for small n , RPA needs a larger basis than DFT for convergence of sums over virtual orbitals. When n is large, RPA+SOSEX is computationally intractable with existing algorithms.

In this paper, we propose a new RPA+SOSEX algorithm to match the computational scaling of DFT and define a self-consistent mean field. The algorithm uses a spatially localized basis, fast summation of the Coulomb kernel, and a low-rank approximation of energy denominators¹⁰. The RPA+SOSEX model is again revised to approximate a higher level of theory: Brueckner coupled-cluster doubles (BCCD) theory¹¹. BCCD applies a nonunitary similarity transformation that produces a non-Hermitian mean field. We replace it with a best Hermitian approximation to preserve the structure of orthogonal orbitals with real orbital energies that is expected of a mean field.

We consider a Hermitian many-electron Hamiltonian with n electrons over αn orbitals in second quantization notation,

$$\hat{H} = E_0 + h_{xy}\hat{a}_x^\dagger\hat{a}_y + \frac{1}{2}V_{xy}\hat{n}_x\hat{n}_y - \frac{1}{2}V_{xx}\hat{n}_x, \quad (1)$$

for raising (\hat{a}_x^\dagger) and number ($\hat{n}_x = \hat{a}_x^\dagger\hat{a}_x$) operators in a basis with indices $\{w, x, y, z\}$ and $V_{xy} = V_{yx}$. Repeated indices in a tensor are summed implicitly unless they appear unpeated in a tensor in the same equation. We define a reference Slater determinant, $|\Phi\rangle$, with an orbital transformation,

$$\hat{a}_x = \phi_{px}\hat{c}_p, \quad \phi_{px}^*\phi_{qx} = \delta_q^p, \quad \hat{c}_i^\dagger|\Phi\rangle = \hat{c}_a|\Phi\rangle = 0. \quad (2)$$

General orbital indices are $\{p, q, r, s\}$, occupied orbital indices are $\{i, j, k, l\}$, and virtual orbital indices are $\{a, b, c, d\}$. With $S_{qx}^0 = \phi_{px}^*\phi_{qx}$, the \hat{H} coefficients in the orbital basis are

$$h_q^p = \phi_{px}^*h_{xy}\phi_{qy}, \quad V_{qs}^{pr} = S_{qx}^0V_{xy}S_{sy}^0. \quad (3)$$

We antisymmetrize tensors with $\tilde{V}_{qs}^{pr} = V_{qs}^{pr} - V_{qs}^{rp}$. BCCD theory approximates the ground state as

$$|\Psi\rangle \approx \exp(\hat{T}_2)|\Phi\rangle, \quad \hat{T}_2 = \frac{1}{2}T_{ij}^{ab}\hat{c}_a^\dagger\hat{c}_b^\dagger\hat{c}_i\hat{c}_j. \quad (4)$$

We enforce partial symmetry constraints: $T_{ij}^{ab} = T_{ji}^{ba}$ but not $T_{ij}^{ab} = -T_{ij}^{ba}$. \tilde{T}_{ij}^{ab} is defined by projection of $\hat{H}|\Psi\rangle = E|\Psi\rangle$,

$$\langle\Phi|\hat{X}\exp(-\hat{T}_2)\hat{H}|\Psi\rangle = E\langle\Phi|\hat{X}\exp(-\hat{T}_2)|\Psi\rangle, \quad (5)$$

for $\hat{X} \in \{1, \hat{c}_i^\dagger\hat{c}_a, \hat{c}_j^\dagger\hat{c}_b\hat{c}_i^\dagger\hat{c}_a\}$. These BCCD equations are

$$\begin{aligned} E - E_0 &= \frac{1}{2}(h_i^i + b_i^i) = h_i^i + \frac{1}{2}\tilde{V}_{ij}^{ij} + \frac{1}{4}\tilde{V}_{ab}^{ij}\tilde{T}_{ij}^{ab}, \\ b_q^p &= h_q^p + \tilde{V}_{iq}^{ip} + (\delta_a^p\delta_q^i h_b^j + \frac{1}{2}\tilde{V}_{ab}^{pj}\delta_q^i - \frac{1}{2}\delta_a^p\tilde{V}_{qb}^{ij})\tilde{T}_{ij}^{ab}, \\ 0 &= b_i^a, \quad R_{ij}^{ab} = \tilde{V}_{ic}^{ak}\tilde{T}_{kj}^{cb} + \tilde{V}_{ik}^{ac}\tilde{T}_{cj}^{kb} + \tilde{V}_{ik}^{ac}\tilde{V}_{cd}^{kl}\tilde{T}_{lj}^{db}, \\ 0 &= \tilde{V}_{ij}^{ab} + b_c^a\tilde{T}_{ij}^{cb} - b_i^k\tilde{T}_{kj}^{ab} + b_c^b\tilde{T}_{ij}^{ac} - b_j^k\tilde{T}_{ik}^{ab} + \tilde{R}_{ij}^{ab} \\ &\quad + \frac{1}{2}\tilde{V}_{cd}^{ab}\tilde{T}_{ij}^{cd} + \frac{1}{2}\tilde{T}_{kl}^{ab}\tilde{V}_{ij}^{kl} + \frac{1}{4}\tilde{T}_{kl}^{ab}\tilde{V}_{cd}^{kl}\tilde{T}_{ij}^{cd}, \end{aligned} \quad (6)$$

where b_q^p is a non-Hermitian Brueckner mean field¹¹. Eq. (6) needs $\mathcal{O}(\alpha^4 n^6)$ operations and $\mathcal{O}(\alpha^2 n^4)$ memory to solve¹².

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We derive RPA+SOSEX by approximating T_{ij}^{ab} with

$$T_{ij}^{ab} \approx -\frac{S_{ix}^a V_{xy} S_{jy}^b}{\omega_{ai} + \omega_{bj}}, \quad S_{ix}^a = S_{ix}^{a0} + S_{iy}^{a0} V_{yz} A_{zx}(\omega_{ai}), \quad (7)$$

for $\omega_{ai} = \epsilon_a - \epsilon_i > 0$, and retaining all terms in Eq. (6) that preserve this form. Only the fourth-order tensor equations are modified, to an antisymmetrized RPA Riccati equation¹³,

$$0 = \tilde{V}_{ij}^{ab} + (\omega_{ai} + \omega_{bj}) \tilde{T}_{ij}^{ab} + \tilde{D}_{ij}^{ab}, \quad (8)$$

$$D_{ij}^{ab} = V_{ic}^{ak} T_{kj}^{cb} + T_{ik}^{ac} V_{cj}^{kb} + T_{ik}^{ac} V_{cd}^{kl} T_{lj}^{db},$$

which is unsymmetrized by removing \sim to define T_{ij}^{ab} fully. The rest of Eq. (6) is an extended Hartree-Fock (HF) theory,

$$E = E_0 + \frac{1}{2} \rho_{xy} (h_{yx} + f_{yx}), \quad f_{xy} \phi_{py} = \epsilon_p \phi_{px}, \quad (9)$$

$$f_{xy} = h_{xy} + v_x \delta_{xy} - \rho_{xy} V_{xy} + \Sigma_{xy},$$

$$\rho_{xy} = \phi_{ix} \phi_{iy}^*, \quad \bar{\rho}_{xy} = \delta_{xy} - \rho_{xy}, \quad v_x = V_{xy} \rho_{yy},$$

that includes a Hermitian correlation correction term,

$$\Sigma_{xy} = \frac{1}{2} (\sigma_{xy} + \sigma_{yx}^* + \bar{\rho}_{xz} \sigma_{zw} \rho_{wy} + \rho_{xz} \sigma_{wz}^* \bar{\rho}_{wy}), \quad (10)$$

$$\sigma_{xy} = \phi_{ax} \phi_{iy}^* (h_b^j + V_{xz} S_{bz}^{j0} - S_{bz}^{j0} V_{zy}) \tilde{T}_{ij}^{ab}.$$

We refer to this model as Brueckner RPA (BRPA).

Eq. (7) enables Eq. (8) to be factored about V_{xy} ,

$$S_{ix}^a V_{xy} S_{jy}^b = (S_{ix}^{a0} + T_{ik}^{ac} S_{cx}^{k0}) V_{xy} (S_{jy}^{b0} + T_{jl}^{bd} S_{dy}^{l0}). \quad (11)$$

S_{ix}^a is defined by equating the two factors and expanding T_{ij}^{ab} ,

$$S_{ix}^a = S_{ix}^{a0} - S_{iy}^a V_{yz} S_{jz}^{b0} / (\omega_{ai} + \omega_{bj}). \quad (12)$$

S_{ix}^{a0} cancels from this equation to define $A_{xy}(\omega_{ai})$,

$$A_{xy}^0(\omega) = -S_{ix}^{a0} S_{ay}^{i0} / (\omega_{ai} + \omega), \quad (13)$$

$$A_{xy}(\omega) = B_{xy}(\omega) + A_{xz}(\omega) V_{zw} B_{wy}(\omega),$$

$$B_{xy}(\omega) = A_{xy}^0(\omega) - S_{iz}^{a0} V_{zw} A_{wx}(\omega_{ai}) S_{ay}^{i0} / (\omega_{ai} + \omega),$$

which has an analytic continuation from ω_{ai} to $\omega \in \mathbb{C}$.

We split $(\omega_{ai} + \omega_{bj})^{-1}$ in $A_{xy}^0(\omega_{ai})$ and $B_{xy}(\omega_{ai})$ using

$$X_{xy}(\omega_{ai}) = \int_{-i\infty}^{i\infty} \frac{d\Omega}{2\pi i} \frac{X_{xy}(\Omega)}{\omega_{ai} - \Omega} \quad \text{for } X \in \{A^0, B\}, \quad (14)$$

$$A_{xy}^0(i\omega) = -\oint_{\Gamma_v} \frac{d\Omega}{2\pi i} \oint_{\Gamma_o} \frac{d\Omega'}{2\pi i} \frac{G_{yx}(\Omega) G_{xy}(\Omega')}{\Omega - \Omega' + i\omega},$$

with closed counterclockwise contours, Γ_v separating ϵ_a from $\epsilon_i - i\omega$, and Γ_o separating ϵ_i from $\epsilon_a + i\omega$, and the mean-field Green's function, $G_{xy}(\omega) = \phi_{px} \phi_{py}^* / (\omega - \epsilon_p)$. We calculate these integrals approximately using numerical quadratures,

$$1/(\omega_{ai} + \omega_{bj}) \approx \Omega_e / [(\omega_{ai} + \omega_e)(\omega_{bj} - \omega_e)], \quad (15)$$

$$\delta_a^p \delta_i^q / (\omega_{ai} + \omega_e) \approx \Omega_{\bar{a}}^e / [(\omega_{\bar{a}} - \epsilon_p)(\omega_{\bar{i}} - \epsilon_q)],$$

for β_1 points, ω_e , indexed by $\{e, f, g\}$, β_2 points, ω_a , indexed by $\{a, b\}$, and β_3 points, ω_i , indexed by $\{i, j\}$. β_1 , β_2 , and β_3 have logarithmic error dependence and weak n dependence¹⁴. We combine \bar{a} and \bar{i} into one index, \bar{p} . We use a permutation of indices, \bar{e} , to manifest symmetry: $\omega_{\bar{e}} = \omega_e^*$ and $\Omega_{\bar{e}} = \Omega_e$.

We approximate Eq. (13) by applying a closure relation,

$$1/[(\omega_{ai} + \omega_e)(\omega_{bj} - \omega_f)] \approx \Delta_g^{ef} / (\omega_{ai} + \omega_g), \quad (16)$$

$$\Delta_g^{e(f \neq e)} = -(\delta_g^e - \delta_g^f) / (\omega_e - \omega_f), \quad \Delta_f^{ee} = -\nabla_f^e,$$

where ∇_f^e are coefficients of a finite difference approximation of $\frac{d}{d\omega}(\omega_{ai} + \omega)^{-1}$ for $\omega = \omega_e$. This induces approximants,

$$X_{xy}(\omega_{ai}) \approx \Omega_e X_{xy}^e / (\omega_{ai} - \omega_e) \quad \text{for } X \in \{A^0, A, B\}, \quad (17)$$

when combined with Eq. (15). The approximant coefficients are $A_{xy}^{e0} = A_{xy}^0(\omega_e)$, $B_{xy}^e = B_{xy}(\omega_e)$, and A_{xy}^e that solve

$$A_{xy}^{e0} \approx -\Omega_{\bar{a}}^e G_{yx}^a G_{xy}^i, \quad G_{xy}^p = G_{xy}(\omega_p), \quad (18)$$

$$A_{xy}^e \approx B_{xy}^e + A_{xz}^e V_{zw} B_{wy}^e - \Omega_f \Delta_g^{ef} A_{xz}^f V_{zw} B_{wy}^g,$$

$$B_{xy}^e \approx A_{xy}^{e0} + \Omega_f \Delta_g^{ef} A_{xz}^f V_{zw} A_{wy}^{g0},$$

which is a reduced form of Eq. (13) for $\omega = \omega_{ai}$.

Eqs. (15) and (16) reveal reduced numerical rank in T_{ij}^{ab} :

$$T_{ij}^{ab} \approx -G_{ax}^a G_{xi}^i \Omega_{\bar{a}}^e U_{xy}^{ef} \Omega_{\bar{b}}^f G_{by}^b G_{jy}^j, \quad (19)$$

$$G_{ax}^a = \phi_{ax}^* / (\omega_{\bar{a}} - \epsilon_a), \quad G_{xi}^i = \phi_{ix} / (\omega_{\bar{i}} - \epsilon_i),$$

$$U_{xy}^{ef} = C_{xz}^{e\bar{g}} \Omega_g V_{zw} C_{yw}^{fg}, \quad C_{xy}^{ef} = \delta_f^e \delta_{xy} + \Omega_g \Delta_e^{fg} V_{xz} A_{zy}^g.$$

Tensor hypercontraction¹⁵ uses a similar form without orbital energy dependence: $T_{ij}^{ab} \approx -\phi_{ax}^* \phi_{ix} U_{xy} \phi_{by}^* \phi_{jy}$.

We apply Eqs. (12), (15), and (19) to simplify σ_{xy} to

$$\sigma_{xy} \approx K_{xz}^i G_{zy}^i - G_{xz}^a K_{zy}^a, \quad \Xi_{xyz}^{ia} = G_{xw}^i G_{wy}^a V_{wz},$$

$$W_{xy}^e = \Omega_e V_{xz} A_{zw}^e V_{wy}, \quad J_{xy}^{ia} = G_{xz}^i h_{zw} G_{wy}^a,$$

$$K_{xy}^a = \Omega_{\bar{a}}^e G_{xy}^i W_{xy}^e + \Omega_{\bar{a}}^f \Omega_{\bar{b}}^f G_{zy}^i U_{xz}^{ef} \Xi_{xyz}^{ib}, \quad (20)$$

$$K_{xy}^i = \Omega_{\bar{a}}^e G_{xy}^a W_{yx}^e + \Omega_{\bar{a}}^f \Omega_{\bar{b}}^f G_{xz}^a U_{zy}^{ef} \Xi_{zyx}^{ib}$$

$$- \Omega_{\bar{a}}^e G_{xy}^a U_{yz}^{ef} \Omega_{\bar{b}}^f J_{zz}^{ib} + \Omega_{\bar{a}}^f \Omega_{\bar{b}}^f G_{xz}^a U_{zy}^{ef} J_{zy}^{ib}.$$

The first (second) term in K_{xy}^i contributes the RPA (SOSEX) correlation energy to E in Eq. (9) through Σ_{xy} . The analogue in second-order Møller-Plesset (MP2) perturbation theory is

$$\sigma_{xy}^0 \approx K_{xz}^{i0} G_{zy}^i - G_{xz}^a K_{zy}^{a0}, \quad \Xi_{xyz}^{e0} = \Omega_e \Omega_{\bar{a}}^e G_{xw}^i G_{wy}^a V_{wz},$$

$$W_{xy}^{e0} = \Omega_e V_{xz} A_{zw}^{e0} V_{wy}, \quad J_{xy}^{e0} = \Omega_e \Omega_{\bar{a}}^e G_{xz}^i h_{zw} G_{wy}^a,$$

$$K_{xy}^{a0} = \Omega_{\bar{a}}^e G_{xy}^i W_{xy}^{e0} + \Omega_{\bar{a}}^f G_{zy}^i V_{xz} \Xi_{xyz}^{e0}, \quad (21)$$

$$K_{xy}^{i0} = \Omega_{\bar{a}}^e G_{xy}^a W_{yx}^{e0} + \Omega_{\bar{a}}^f G_{xz}^a V_{zy} \Xi_{zyx}^{e0}$$

$$- \Omega_{\bar{a}}^e G_{xy}^a V_{yz} J_{zz}^{e0} + \Omega_{\bar{a}}^f G_{xz}^a V_{zy} J_{zy}^{e0},$$

combined with HF orbitals and energies defined by replacing $f_{xy} \phi_{py} = \epsilon_p \phi_{px}$ in Eq. (9) with $(f_{xy} - \Sigma_{xy}) \phi_{py} = \epsilon_p \phi_{px}$.

Like HF and DFT, BRPA is a self-consistent field theory, with the added burden of calculating σ_{xy} . In a conventional algorithm, we iteratively solve Eq. (12) for S_{ix}^a and calculate σ_{xy} from Eq. (10). In a fast algorithm, we iteratively solve Eq. (18) for A_{xy}^e and calculate σ_{xy} from Eq. (20). We assign $\rho_x \mapsto V_{xy} \rho_y$ a cost of $\alpha \gamma n$ operations, where γ is reduced by a fast summation method. Both algorithms improve upon the $\mathcal{O}(\alpha^3 n^5)$ operations and $\mathcal{O}(\alpha^2 n^4)$ memory cost of the known RPA+SOSEX algorithm⁴. Table I summarizes their costs¹⁶.

TABLE I. Leading-order, per-iteration floating-point costs of tensor formation¹⁶ for two MP2 algorithms and two BRPA algorithms.

Tensor	Operations	Memory
Conventional MP2		$2\alpha^2 n^2$
σ_{xy}^0	$4\alpha^3 n^5$	$\alpha^2 n^2$
Conventional BRPA		$2\alpha^2 n^2$
S_{ix}^a	$4\alpha^3 n^5$	$\alpha^2 n^3$
σ_{xy}	$6\alpha^3 n^5$	$\alpha^2 n^2$
Fast MP2		$2\alpha^2 n^2 + \alpha(\beta_2 + \beta_3)n$
A_{xy}^{e0}	$\alpha^2 \beta_1 \beta_2 \beta_3 n^2$	$\frac{1}{2} \alpha^2 \beta_1 n^2$
J_{xy}^{e0}	$2\alpha^3 \beta_2 \beta_3 n^3 + 2\alpha^2 \beta_1 \beta_2 \beta_3 n^2$	$\alpha^2 \beta_1 n^2$
K_{xy}^{p0}	$2\alpha^3 \beta_1 (2\beta_2 + 2\beta_3 + \gamma) n^3 + 8\alpha^2 \beta_1 \beta_2 \beta_3 n^2$	$\alpha^2 (\beta_2 + \beta_3) n^2$
σ_{xy}^0	$2\alpha^3 (\beta_2 + \beta_3) n^3$	$\alpha^2 n^2$
Fast BRPA		$2\alpha^2 n^2 + \alpha(\beta_1 \beta_2 + \beta_1 \beta_3)n$
A_{xy}^e	$6\alpha^3 \beta_1 n^3 + 2\alpha^2 \beta_1 (3\beta_1 + \gamma) n^2$	$\alpha^2 \beta_1 n^2$
B_{xy}^e	$6\alpha^3 \beta_1 n^3 + 2\alpha^2 \beta_1 (3\beta_1 + \gamma) n^2$	$\alpha^2 \beta_1 n^2$
U_{xy}^{ef}	$\mathcal{O}(\alpha^3 \beta_1^2 n^3 + \alpha^2 \beta_1^2 (\beta_1 + \gamma) n^2)$	$\frac{1}{2} \alpha^2 \beta_1^2 n^2$
J_{xy}^{ia}	$2\alpha^3 \beta_2 \beta_3 n^3$	$\alpha^2 \beta_2 \beta_3 n^2$
K_{xy}^p	$2\alpha^3 [(4\beta_1 + \gamma) \beta_2 \beta_3 + \beta_1^2 (\beta_2 + \beta_3)] n^3$	$\alpha^2 (\beta_2 + \beta_3) n^2$
σ_{xy}	$2\alpha^3 (\beta_2 + \beta_3) n^3$	$\alpha^2 n^2$

The conventional and fast algorithms also apply to MP2. Intermediate calculation of σ_{xy}^0 enables orbital optimizations such as in the BCC2 model¹⁷. By utilizing fast summation of V_{xy} , the fast MP2 algorithm improves upon the $\mathcal{O}(\alpha^4 n^4)$ cost of the previous best algorithm¹⁸. Additional approximations such as orbital localization¹⁹ and stochastic sampling^{20,21} can reduce MP2 costs even further and achieve linear scaling.

We test BRPA on a small problem that is difficult for both DFT²² and RPA²³: the dissociation of H_2 . H_2 is an extended Hubbard model ($\alpha = n = 2$) in the zero-differential-overlap (ZDO) approximation²⁴, which fits the form of Eq. (1) for

$$\mathbf{h} = \begin{bmatrix} \mu & 0 & -t & 0 \\ 0 & \mu & 0 & -t \\ -t & 0 & \mu & 0 \\ 0 & -t & 0 & \mu \end{bmatrix}, \quad \mathbf{V} = \begin{bmatrix} U & U & V & V \\ U & U & V & V \\ V & V & U & U \\ V & V & U & U \end{bmatrix}. \quad (22)$$

Its HF, MP2, BRPA, and exact (BCCD) total energies are¹⁶

$$\begin{aligned} E_{\text{HF}} &= E_0 + 2(\mu - t) + \frac{1}{2}(U + V), \\ E_{\text{MP2}} &= E_{\text{HF}} - \frac{(U-V)^2}{16t+8V}, \quad E_{\text{BRPA}} = E_{\text{HF}} - \frac{(U-V)^2}{16t+8U}, \\ E &= E_0 + 2\mu + \frac{1}{2}(U + V) - \sqrt{4t^2 + \frac{1}{4}(U - V)^2}. \end{aligned} \quad (23)$$

With total energies of H_2^+ , $E_+ = E_0 + \mu - t$, and H_2^{++} , E_0 , we invert $\{E_+, E, E_{\text{HF}}, E_{\text{MP2}}\}$ to determine $\{\mu, t, U, V\}$. These parameters are fit to accurate energies¹⁶ to evaluate the BRPA solution semiempirically in Fig. 1. All approximations fail at dissociation. Significant reduction of the orbital energy gaps improves BRPA, consistent with smaller RPA+SOSEX errors in calculations based on semilocal DFT⁷ compared with HF²⁵. The BRPA mean field approximates quasiparticle gaps²⁶ that are systematically underestimated by semilocal DFT.

BRPA is a poor approximation of BCCD theory. A change of mean field can reduce errors in the total energy, but further reduces fidelity to the underlying theory. A variational theory of RPA+SOSEX optimized over mean fields may resolve this discrepancy, but first it must repair known instabilities²⁷.

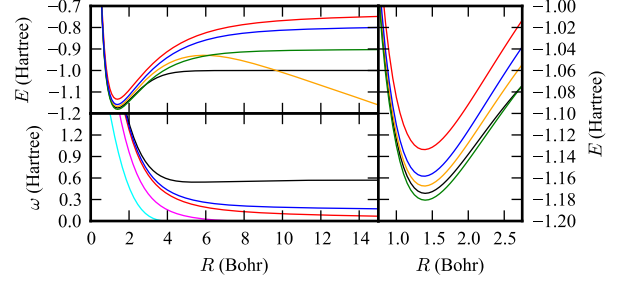


FIG. 1. Total energy, E , and virtual-occupied orbital energy gap, ω , of H_2 as a function of interatomic distance, R . Shown are the exact (black), HF (red), MP2 (orange), B3LYP (green), and BRPA (blue) results. For $R < 4$, RPA+SOSEX is exact with a tuned gap (cyan). Gaps are model-derived, with the exact gap from BCCD theory, and a noninteracting gap (magenta), $2t$, indicative of semilocal DFT.

Efficient BRPA calculations must minimize α , β_1 , β_2 , β_3 , and γ . Minimizing β_1 , β_2 , and β_3 is a well-defined problem of optimizing integration quadrature. Minimizing γ requires further development of fast Poisson solvers. To relate Eq. (1) to the standard quantum chemistry Hamiltonian, we interpret x as a real space index and use an $\alpha \rightarrow \infty$ limit to recover the continuum. ϕ_{px} is approximated in a finite basis that restricts orbitals in number and accuracy. BRPA will converge slowly in the size of this basis, similar to other electron correlation models. There are multiple interpretations and solutions: as a slow virtual orbital summation it is corrected with remainder modeling²⁸, and as a cusp in the many-electron wavefunction it is corrected with cusp modeling²⁹. With G_{xy}^p calculated as shifted matrix inverses of f_{xy} and ρ_{xy} calculated with

$$\rho_{xy} = \oint_{\Gamma_0} \frac{d\Omega}{2\pi i} G_{xy}(\Omega) \approx \Omega_i G_{xy}^i, \quad (24)$$

the direct use of orbitals, including virtual orbital summation, is removed from BRPA. Basis convergence generalizes to an operator approximation problem for G_{xy}^p and A_{xy}^e . Similar to wavefunction cusps, G_{xy}^p and A_{xy}^e both have singularities that are poorly approximated in an orbital basis. They need direct modeling to reduce the basis set size required to approximate the remaining smooth operator. Direct approximation of G_{xy}^p and A_{xy}^e also enables use of operator-specific basis sets with more flexibility than a single atomic orbital basis set.

Fast RPA calculations enable a compromise between DFT efficiency and coupled-cluster accuracy. The $\mathcal{O}(n^3)$ cost of an RPA correlation model is much greater than the $\mathcal{O}(n)$ cost of a standard DFT model and much less than the $\mathcal{O}(n^6)$ cost of the BCCD model. It matches the $\mathcal{O}(n^3)$ scaling of mean field calculations that generate the physical inputs needed by these models. Whether an RPA model can surpass the accuracy of standard DFT models and approach BCCD accuracy remains to be determined. Several open problems also remain before efficient implementation of RPA calculations on real materials attain practically useful performance.

I thank Jay Sau, Norm Tubman, Jeff Hammond, Andrew Baczewski, Rick Muller, and Toby Jacobson for many useful discussions. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a

wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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SUPPLEMENTARY MATERIAL

I. TENSOR FORMATION

Efficient evaluation of tensor equations requires a careful ordering of operations and choice of intermediate variables. To account for the costs in Table I of the paper, we reduce the calculations to pseudocode where each addition, subtraction, multiplication, and division is a floating-point operation and each floating-point number is a unit of memory. X and Y are workspace tensors that are reindexed as needed. Workspace sizes are listed next to the algorithm names in Table I.

Conventional MP2:

```

 $\sigma_{xy}^0 \leftarrow 0$ 
for each  $a$  do
   $X_{jx} \leftarrow V_{xy}\phi_{jy}\phi_{ay}^*$ 
  for each  $i$  do
     $Y_{jx} \leftarrow X_{jx}\phi_{ix} - X_{ix}\phi_{jx}$ 
     $X_j^b \leftarrow \phi_{bx}^* Y_{jx}$ 
     $X_j^b \leftarrow X_j^b / (\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j)$ 
     $Y_{jx} \leftarrow X_j^b \phi_{bx}$ 
     $Y_x \leftarrow Y_{jx}\phi_{jx}^*$ 
     $X \leftarrow h_b^j X_j^b$ 
     $X_x \leftarrow V_{xy} Y_y$ 
     $\sigma_{xy}^0 \leftarrow \sigma_{xy}^0 + \phi_{ax}\phi_{iy}^*(X + X_x - X_y)$ 
  end for
end for

```

Conventional BRPA:

```

for each  $a$  and  $i$  do
   $X_x \leftarrow V_{xy}S_{iy}^a(\text{old})$ 
   $X_j^b \leftarrow -X_x S_{jx}^b(\text{old})$ 
   $X_j^b \leftarrow X_j^b / (\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j)$ 
   $X_{jx} \leftarrow X_j^b \phi_{bx}$ 
   $S_{ix}^a(\text{new}) \leftarrow \phi_{ax}^* \phi_{ix} + X_{jx}\phi_{jx}^*$ 
end for.

```

```

 $\sigma_{xy} \leftarrow 0$ 
for each  $a$  do
   $X_{jx} \leftarrow V_{xy}S_{jy}^a$ 
  for each  $i$  do
     $X_j^b \leftarrow X_{jx}S_{ix}^b - X_{ix}S_{jx}^b$ 
     $X_j^b \leftarrow X_j^b / (\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j)$ 
     $Y_{jx} \leftarrow X_j^b \phi_{bx}$ 
     $Y_x \leftarrow Y_{jx}\phi_{jx}^*$ 
     $X \leftarrow h_b^j X_j^b$ 
     $X_x \leftarrow V_{xy} Y_y$ 
     $\sigma_{xy} \leftarrow \sigma_{xy} + \phi_{ax}\phi_{iy}^*(X + X_x - X_y)$ 
  end for
end for

```

Fast MP2:

for each x and y **do**

$$X_{xy}^{ai} \leftarrow G_{yx}^a G_{xy}^i$$

$$A_{xy}^{e0} \leftarrow -\Omega_{ai}^e X_{xy}^{ai}$$

end for

$$J_{xy}^{e0} \leftarrow 0$$

for each a **do**

$$X_{xy} \leftarrow h_{xz} G_{zy}^a$$

for each i **do**

$$Y_{xy} \leftarrow G_{xz}^i X_{zy}$$

$$J_{xy}^{e0} \leftarrow J_{xy}^{e0} + \Omega_e \Omega_{ai}^e Y_{xy}$$

end for

end for

$$K_{xy}^{p0} \leftarrow 0$$

for each e **do**

$$X_{xy} \leftarrow A_{xz}^{e0} V_{zy} \Omega_e$$

$$Y_{xy} \leftarrow V_{xz} X_{zy}$$

$$X_y \leftarrow V_{yz} J_{zz}^{e0}$$

for each x and y **do**

$$X^i \leftarrow Y_{xy} G_{xy}^i$$

$$X^a \leftarrow (Y_{yx} - X_y) G_{xy}^a$$

$$K_{xy}^{a0} \leftarrow K_{xy}^{a0} + \Omega_{ai}^e X^i$$

$$K_{xy}^{i0} \leftarrow K_{xy}^{i0} + \Omega_{ai}^e X^a$$

end for

end for

for each z and e **do**

$$X_{xz}^a \leftarrow \Omega_e \Omega_{ai}^e G_{zx}^i$$

$$X_x^i \leftarrow \Omega_{ai}^e G_{xz}^a$$

for each x **do**

$$X_y \leftarrow V_{xz} X_y^i G_{xy}^i$$

$$Y_y \leftarrow V_{yw} X_w$$

$$K_{xy}^{a0} \leftarrow K_{xy}^{a0} + X_y^a Y_y$$

end for

for each y **do**

$$X_x \leftarrow X_x^a G_{xy}^a$$

$$Y_x \leftarrow V_{xw} X_w$$

$$Y_x \leftarrow V_{zy} (Y_x + J_{zy}^{e0})$$

$$K_{xy}^{i0} \leftarrow K_{xy}^{i0} + X_x^i Y_x$$

end for

end for

$$\sigma_{xy}^0 \leftarrow K_{xz}^{i0} G_{zy}^i - G_{xz}^a K_{zy}^{a0}$$

Fast BRPA:

$$A_{xy}^e(\text{new}) \leftarrow B_{xy}^e$$

for each e **do**

$$X_{xy} \leftarrow \Omega_f A_{xy}^f(\text{old})(1 - \delta_f^e) / (\omega_e - \omega_f + \delta_f^e)$$

$$Y_{xy} \leftarrow X_{xz} V_{zy}$$

$$X_{xy} \leftarrow A_{xz}^e(\text{old}) V_{zy}$$

$$A_{xy}^e(\text{new}) \leftarrow A_{xy}^e(\text{new}) + Y_{xz} B_{zy}^e$$

$$Y_{xy} \leftarrow X_{xz} B_{zy}^e$$

$$A_{xy}^f(\text{new}) \leftarrow A_{xy}^f(\text{new}) + \Omega_e Y_{xy} / (\omega_e - \omega_f + \delta_f^e \Omega_e)$$

$$Y_{xy} \leftarrow \Omega_e \nabla_f^e B_{xy}^f$$

$$A_{xy}^e(\text{new}) \leftarrow A_{xy}^e(\text{new}) + X_{xz} Y_{zy}$$

end for

$$B_{xy}^e \leftarrow A_{xy}^{e0}$$

for each e **do**

$$X_{xy} \leftarrow \Omega_f A_{xy}^f(1 - \delta_f^e) / (\omega_e - \omega_f + \delta_f^e)$$

$$Y_{xy} \leftarrow X_{xz} V_{zy}$$

$$X_{xy} \leftarrow A_{xz}^e V_{zy}$$

$$B_{xy}^e \leftarrow B_{xy}^e - Y_{xz} A_{zy}^{e0}$$

$$Y_{xy} \leftarrow X_{xz} A_{zy}^{e0}$$

$$B_{xy}^f \leftarrow B_{xy}^f - \Omega_e Y_{xy}(1 - \delta_f^e) / (\omega_e - \omega_f + \delta_f^e)$$

$$Y_{xy} \leftarrow \Omega_e \nabla_f^e A_{xy}^{f0}$$

$$B_{xy}^e \leftarrow B_{xy}^e - X_{xz} Y_{zy}$$

end for

```

 $J_{xy}^{ia} \leftarrow 0$ 
for each  $\underline{a}$  do
   $X_{xy} \leftarrow h_{xz} G_{zy}^a$ 
  for each  $\underline{i}$  do
     $J_{xy}^{ia} \leftarrow G_{xz}^i X_{zy}$ 
  end for
end for

 $K_{xy}^p \leftarrow 0$ 
for each  $\underline{e}$  do
   $X_{xy} \leftarrow A_{xz}^e V_{zy} \Omega_e$ 
   $Y_{xy} \leftarrow V_{xz} X_{zy}$ 
  for each  $\underline{i}$  do
     $X_{xy} \leftarrow Y_{xy} G_{xy}^i$ 
     $K_{xy}^a \leftarrow K_{xy}^a + \Omega_{ai}^e X_{xy}$ 
  end for
   $X_z^f \leftarrow \Omega_{bz}^f J_{zz}^{ib}$ 
   $X_y \leftarrow U_{yz}^{ef} X_z^f$ 
   $Y_{xy} \leftarrow Y_{xy} - X_x$ 
  for each  $\underline{a}$  do
     $X_{xy} \leftarrow Y_{yx} G_{xy}^a$ 
     $K_{xy}^i \leftarrow K_{xy}^i + \Omega_{ai}^e X_{xy}$ 
  end for
end for

for each  $\underline{z}$  do
   $X_y^{fb} \leftarrow \Omega_{bz}^f G_{zy}^i$ 
  for each  $\underline{x}$  do
     $X_y^{bj} \leftarrow G_{xw}^j G_{wz}^b V_{wy}$ 
     $X_y^{fj} \leftarrow X_y^{fb} X_y^{bj}$ 
    for each  $\underline{y}$  do
       $X_{xy}^{ej} \leftarrow U_{xz}^{ef} X_y^{fj}$ 
       $K_{xy}^a \leftarrow K_{xy}^a + \Omega_{aj}^e X_{xy}^{ej}$ 
    end for
  end for
end for

for each  $\underline{z}$  do
   $X_x^{ej} \leftarrow \Omega_{aj}^e G_{xz}^a$ 
  for each  $\underline{y}$  do
     $X_x^{bj} \leftarrow G_{zw}^j G_{wy}^b V_{wx} + J_{zy}^{jb}$ 
     $X_x^{eb} \leftarrow X_x^{ej} X_x^{bj}$ 
    for each  $\underline{x}$  do
       $X^{fb} \leftarrow U_{zy}^{ef} X_x^{eb}$ 
       $K_{xy}^i \leftarrow K_{xy}^i + \Omega_{bi}^f X^{fb}$ 
    end for
  end for
end for

 $\sigma_{xy} \leftarrow K_{xz}^i G_{zy}^i - G_{xz}^a K_{zy}^a$ 

```

II. H₂ DISSOCIATION

For the model in Eq. (22), we choose reference orbitals

$$\phi = \frac{1}{\sqrt{2}} \begin{bmatrix} i & j & a & b \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & -1 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}, \quad (1)$$

where $\{i, j\}$ label the two occupied orbitals and $\{a, b\}$ label the two virtual orbitals. The nonzero matrix elements are

$$\begin{aligned} h_i^i &= h_j^j = \mu - t, & h_a^a &= h_b^b = \mu + t, \\ V_{aa}^{ii} &= V_{bb}^{jj} = -V_{ab}^{ij} = \frac{1}{2}(U - V), \\ V_{ii}^{ii} &= V_{ib}^{ib} = V_{ia}^{ia} = V_{ij}^{ij} = \frac{1}{2}(U + V), \end{aligned} \quad (2)$$

where the last case applies to all V_{pq}^{pq} matrix elements.

The total energy and mean-field BCCD equations are

$$\begin{aligned} E &= E_0 + 2(\mu - t) + V + \frac{1}{2}(U - V)(1 - T), \\ \omega &= 2t + U - (U - V)(1 - T), \end{aligned} \quad (3)$$

where $T = \tilde{T}_{ij}^{ab}$ and ω is the orbital energy difference between occupied and virtual orbitals. These are also the complete HF equations if $T = 0$. In BCCD theory, T is the solution to

$$0 = 2(\omega - U)T - \frac{1}{2}(U - V)(1 - 4T + 3T^2). \quad (4)$$

The RPA+SOSEX approximation of this condition is

$$0 = 2\omega T - \frac{1}{2}(U - V)(1 - 4T + 4T^2), \quad (5)$$

which reduces the 4-by-4 matrix RPA Riccati equation on T_{ij}^{ab} to a direct condition on T by using matrix symmetries. Further solution of these equations is straightforward algebra.

ACKNOWLEDGMENTS

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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